DETECTION OF COMPLEXES IN SOLUTION BY A VOLUME-CHANGE METHOD

BY

PHILIP SCHAFFNER BAKER

A.B., DePauw University, 1938
M.A., University of Arkansas, 1939

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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ACKNOWLEDGEMENT

The author would like to express his sincere appreciation to Professor J. H. Reedy for many timely suggestions and for much patient help during the course of this investigation.

Introduction

The physical properties of solutions have been extensively studied as a basis for determining the constituents of solutions of electrolytes. As a general rule, these studies have indicated extensive dissociation in the so-called strong electrolytes. Many electrolytes however, show some association, suggesting that ionization is not complete, and even that single ions have combined with each other to form complexes. The interpretations of the properties studied are in an agreement that is often more qualitative than quantitative. Hence every addition to the knowledge in this field helps to make the problem clearer and more intelligible.

The property of specific volumes has seldom been used in the study of solutions. Early investigators hoped that a definite specific volume could be assigned to each atom or radical, so that the average specific volumes of solutions could be calculated by the additivity principle. Nernst[1] and Traube[2] showed that volumes in reacting systems were not additive, and the promoters gave up their studies, probably in disappointment that they did not bear out the cherished theories. At any rate, this approach to the problem of solutions has been neglected during recent years.

Lately there have arisen sharp differences in opinions with regard to the composition of certain complex ions. Different studies have indicated different ionic formulas, particularly in the case of the ferric thiocyanate, and it seemed to the author that a study of the volume changes involved in the formation of such complexes might lend evidence to the probability of one view or another.

The volume changes met in reactions involving complex formation are considerable, and may be followed by a manometer attached to a closed apparatus in a constant temper-

ature bath. In some cases the changes are smaller, and the method offers little in informational return. The method is limited to reactions where there is no precipitation and no gas formation. (Gas formation causes a gradual "creeping" in the level of the manometer fluid.)

Before applying this method to any individual reactions, the theoretical limitations of the method should be defined. Assuming arbitrary values for the specific volume (or any other property) of the ions and molecules involved, volume-composition diagrams of simple reactions were calculated. For the formation of a stable compound (complex), 0% ionized, a curve with a sharp break at the theoretical or stoichiometric endpoint was obtained. That is, the composition of the complex was shown on the composition axis. Using the same reaction, but assuming an ionization of 50%, a flexure was obtained instead of a break. Furthermore this flexure did not indicate the proper composition of the complex, but rather a composition high in percent of the ion in excess. (In titrating, the apparent endpoint came too soon). It was evident that for dissociation of more than 50%, the apparent end point would be still further displaced, and the flexure would become so indistinct as to be hardly detectable. In the arbitrary system studied, this method would not show a noticeable flexure for dissociations greater than, say, 75%. In general, then, the method is limited to very stable compounds or complexes. For complexes of moderate stability, the composition indicated is incorrect. For complexes of only 25% associated ion, the existence of the complex may not be shown at all. Of course, a theoretical consideration such as this is not strictly accurate, but is at least indicative of the trends.

Experimental

Lead Acetate.—The first complex to be investigated was the one formed when Pb^{++} ions are titrated with increasing amounts of acetate solution. Here a break occurs in the graph at the composition of Pb^{++}: $2C_2H_3O_2^-$. No evidence was found for the existence of an anion of higher acetate content,

which is in agreement with the results of Fox[3]. The possibility of its existence, as postulated by Blomberg[4], remains, however, for the method is rigorously applicable only to stable complexes. Pb $(C_2H_3O_2)_4^{--}$ may exist, but it would be highly dissociated into Pb $(C_2H_3O_2)_2$ and $C_2H_3O_2^-$.

Barium Chloride.—Some authors[5,6] have suggested complexes such as Na_2BaCl_4 and H_4MgCl_6. When we titrated $BaCl_2$ with NaCl, a straight line was obtained. The interpretation is similar to that for $Pb(C_2H_3O_2)_4^{--}$—only a small amount of Na_2BaCl_4.

Ferric Salts.—Upon titrating Fe^{+++} solutions with CNS^-, F^- and $PO_4^{\equiv}$ different forms of curves were obtained, depending not only upon the concentration of the Fe^{+++} solution, but also upon the anion combined with the Fe^{+++}. The simplest explanation of these differences is that these salts are not completely ionized, but exist as complexes of greater or less stability. The Fe^{+++}—CNS^- complex differs from these others only in its stability. The position of the flexure in the curve is without much significance, for the complexes are decidedly not stable (as is indicated by the decolorizing of ferric thiocyanate when F^- or $PO_4^{\equiv}$ is added.) Furthermore, the Fe^{+++} ion is hydrated, and undoubtedly the water molecules enter into the composition of these complexes just as would be predicted from the Werner theory[7].

So far as this method goes, Fe^{+++} ion does not combine with CNS^- (or F^- or $PO_4^{\equiv}$) to form any single complex. It is more reasonable to assume that every stage in the series Fe^{+++}, $Fe(CNS)^{++}$ . . . . . $Fe(CNS)_5^{--}$, $Fe(CNS)_6^{---}$ exists, in dynamic equilibrium with the others. The hydration of the ions adds more to the complexity of the solution. The physical properties of such mixtures would not conform to any simple mathematical expression, and no definite formula can be assigned to the complex, for it is a mixture of complex ions just as are the ammines of Co and Ni. This explains, perhaps, why different formulas[8,9] are suggested in the literature.

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Vita

The author was born in Minneapolis, Minnesota on November 30, 1916. He attended grammar school in Syracuse and was graduated from high school in Baldwin, New York. He attended Occidental College for one year, Antioch College for two years, and received his Bachelor of Arts degree from DePauw University in 1938. The following year was spent as Coulter W. Jones Scholar at the University of Arkansas where he received the degree of Master of Arts in 1939. After remaining out of school for one year, he entered the Graduate School of the University of Illinois, where to date he has held assistantships in inorganic and analytical chemistry.

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